REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
	Technical Papers	

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) (661) 275-5015
Unclassified	Unclassified	Unclassified	A		

1122 028

MEMORANDUM FOR PRS

12 May 1999

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0075**
Christe (ERC) et. al., "High Energy Density Materials: Synthesis and Characterization of the
Pentanitrogen…"

Received: 25 May 99   **Journal Submission**   (Statement A)

High Energy Density Materials: Synthesis and Characterization of the Pentanitrogen (1+) Cation, N_5^+, a Novel Homoleptic Polynitrogen Ion [**]

Karl O. Christe,[*] William W. Wilson, Jeffrey A. Sheehy, and Jerry A. Boatz

Dedicated to Professor George Olah on the occasion of his 72nd birthday

Polynitrogen compounds are of significant interest as high energy density materials (HEDM) for propulsion or explosive applications.[1-3] In spite of numerous theoretical studies predicting that certain all-nitrogen compounds might be stable, however, only a few unsuccessful experimental studies aimed at their actual synthesis have been undertaken.[4] Presently, only two homoleptic polynitrogen species are known which can be prepared on a macroscopic scale: dinitrogen, N_2, which was independently isolated in pure form from air in 1772 by Rutherford, Scheele, and Cavendish, and the azide anion, N_3^-, discovered in 1890 by Curtius.[5] Other species, such as $N_3^{\cdot}$, N_3^+, and N_4^+, have been observed only as free gaseous or matrix-isolated ions or radicals.[6-8] In view of the extensive theoretical studies indicating that molecules such

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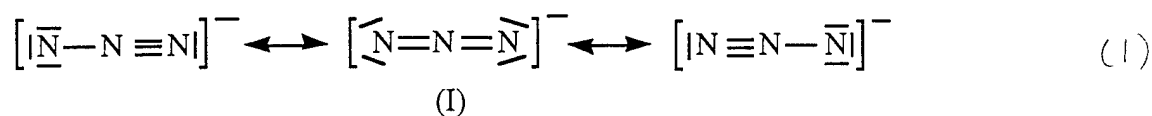   Los Angeles, CA 90089 (USA)

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as N_4 (T_d), N_8 (O_h), $N(N_3)_2^-$, $N(N_3)_3$, and $N(N_3)_4^+$ are vibrationally stable, the lack of a single successful synthesis of a new species on a macroscopic scale is surprising and may be a testament to the great experimental difficulties resulting from their high endothermicities, which give rise to instability and unpredictable explosiveness.
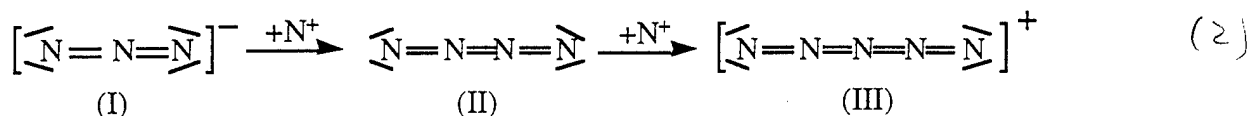
The high energy content of polynitrogen candidates stems from the N-N single and double bonds they possess, with average bond energies of 38.2 and 99.9 kcal/mol, respectively, that are much less than one-third or two-thirds the N_2 triple bond energy of 228 kcal/mol.[9] Therefore, any transformation of a polynitrogen compound to N_2 molecules is accompanied by a very large energy release, and any new metastable polynitrogen compound will be isolable and manageable only if it possesses a sufficiently large energy barrier to decomposition.

In view of the dearth of either known or potential new synthetic pathways for the construction of homoleptic polynitrogen rings or polycycles, and because many chain- or branch-type polynitrogen compounds are calculated to be lower in energy than their cyclic or polycyclic isomers,[3] our efforts are focused on the synthesis of catenated polynitrogen species, which may be more readily accessible. The weakest link in a chain always determines its overall strength, so it is imperative to search for target compounds devoid of any isolated N-N single bonds that cannot gain partial multiple-bond character through resonance with neighboring bonds.

The building principle and unique resonance stabilization of the well known and exceptionally stable azide anion (I) (ᵃᵖ shown in structure 1)

$$\left[|\overline{\underline{N}}-N\equiv N| \right]^- \longleftrightarrow \left[\overline{N}=N=\overline{N} \right]^- \longleftrightarrow \left[|N\equiv N-\overline{\underline{N}}| \right]^- \qquad (1)$$
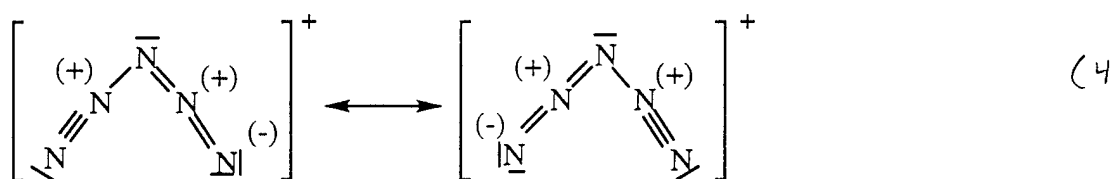
(I)

2

in which each N-N bond has full double bond character, might be further extended by the addition of nitrogens containing only four valence electrons, that is, N^+ ions. This leads first to neutral N_4 (II) and then to the N_5^+ cation (III): ⌐ in structure 2

$$\left[\overset{\frown}{N} = N = \overset{\frown}{N} \right]^- \xrightarrow{+N^+} \overset{\frown}{N} = N = N = \overset{\frown}{N} \xrightarrow{+N^+} \left[\overset{\frown}{N} = N = N = N = \overset{\frown}{N} \right]^+ \qquad (2)$$

$$\qquad\quad (I) \qquad\qquad\qquad (II) \qquad\qquad\qquad\qquad (III)$$

Although structures (II) and (III) contain, like azide, only cumulated linear N=N double bonds, the electronic charge distributions

$$\overset{(-)\quad (+)\quad (-)}{\left[\overset{\frown}{N} = N = \overset{\frown}{N} \right]^-} \qquad \overset{(-)\quad (+)\quad (+)\quad (-)}{\overset{\frown}{N} = N = N = \overset{\frown}{N}} \qquad \overset{(-)\quad (+)\quad (+)\quad (+)\quad (-)}{\left[\overset{\frown}{N} = N = N = N = \overset{\frown}{N} \right]^+} \qquad (3)$$

are only favorable for N_3^-, whereas the neighboring positive charges render structures (II) and (III) energetically unfavorable. However, the problem of neighboring equal-sign charges can be remedied for N_5^+ with the following resonance structures, which result in a bent structure of C_{2v} symmetry with a bond order of 1.5 for the central N-N bonds.

$$\left[\begin{array}{c} \overset{\_}{N} \\ (+) \diagup \text{ } \diagdown (+) \\ N \text{   } N \\ \diagup \text{   } \diagdown (-) \\ N \text{   } N \end{array} \right]^+ \longleftrightarrow \left[\begin{array}{c} \overset{\_}{N} \\ (+) \diagup \text{ } \diagdown (+) \\ N \text{   } N \\ (-) \diagup \text{   } \diagdown \\ N \text{   } N \end{array} \right]^+ \qquad (4)$$

For linear N_4, analogous structures cannot be written, and, therefore, N_5^+ was chosen as the prime target of our synthesis program.

Only one previous report on N_5^+ was found in the literature, a theoretical study of a series of ABCBA-type compounds by Pyykkö and Runeberg.[10] Based on MP2/6-31G* calculations, they predicted a planar C_{2v}-symmetry structure with a BCB angle of 110.7°. The possible synthesis of N_5^+ was considered in 1992 by G. Rasul in his Ph.D. proposal at the University of

Southern California, but it was not pursued.[11]   We report now the synthesis and

characterization of $N_5^+AsF_6^-$, which constitutes only the third known compound containing a

homoleptic polynitrogen moiety that is preparable on a macroscopic scale.

Theoretical calculations were used to predict whether the candidate is vibrationally stable,

and spectroscopic properties (for example, infrared, Raman, and NMR) were calculated to aid in

the identification and characterization. For N_5^+, these calculations predict the stable C_{2v} structure

depicted in Figure 1.

In designing a synthesis, it is useful to find energetic starting materials that already possess

the energy-enhancing weakened bonds, the required formal charges, and suitable ligands that allow

for an exothermic and facile coupling reaction of the starting materials. If the target molecule is a

cation such as N_5^+, the presence of a formal positive charge in one of the starting materials is very

important in view of the high first ionization potential of N_2 (359 kcal/mol). ~~Scheme 1~~ Structure 5 shows

that the N_2F^+ cation and HN_3 are ideal starting materials for the synthesis of N_5^+ because they

already possess the desired types of bonds, N_2F^+ provides the formal positive charge, and in

view of the weak N-F and strong H-F bond, the H-F elimination reaction is expected to be

exothermic.

$$\left[\,|\overline{\underline{F}}-N\equiv N\,|\,\right]^+ + H\overline{N}=N=\overline{N}\longrightarrow \left[\begin{array}{c}\overline{N}\\N\diagdown\diagup N\\N\diagup\qquad\diagdown N\,|\end{array}\right]^+ + HF \qquad (5)$$
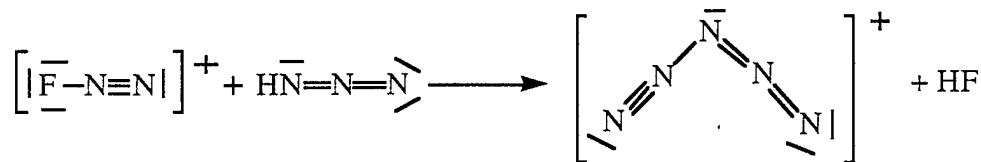
~~(SCHEME 1)~~

A final important point is the need for a reaction medium that offers good solubility at low

temperatures, can act as a heat sink for the exothermic reaction, and can stabilize a product that is

potentially very shock sensitive. For N_5^+, anhydrous HF was chosen because of its high dipole

moment, low melting point (-80 °C), and high volatility.

Application of these principles led to a surprisingly straighforward synthesis of N_5^+

according to

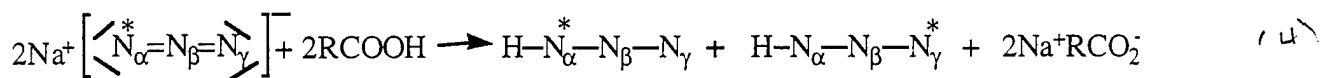$$N_2F^+AsF_6^- + HN_3 \xrightarrow[-78°C]{HF} N_5^+AsF_6^- + HF \qquad (1)$$
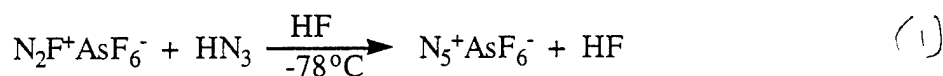
A small excess of HN_3 was used to ensure complete conversion of the $N_2F^+AsF_6^-$. The only

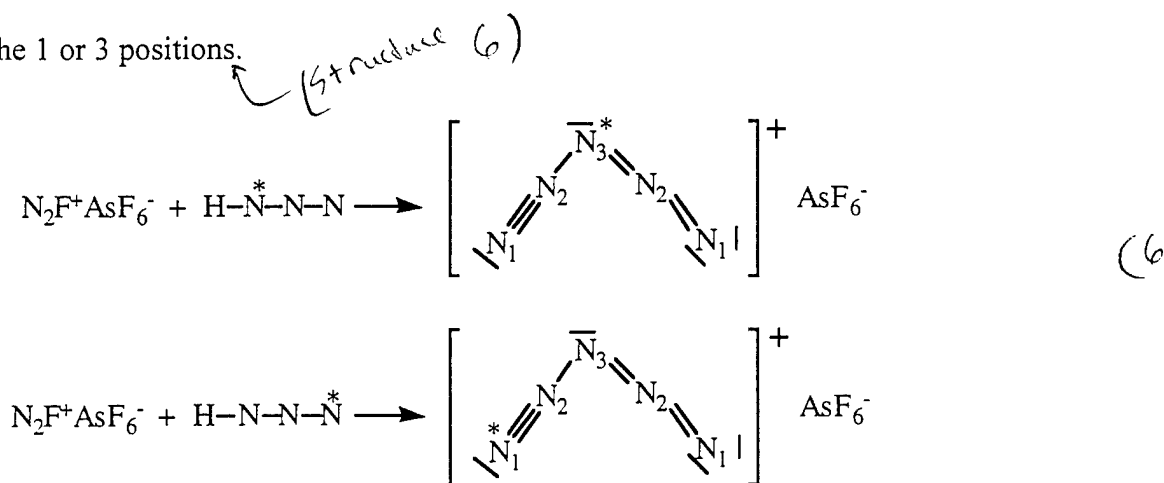detectable by-product less than 20 mol% of protonated HN_3,[12] formed according to

$$HN_3 + HF + AsF_5 \xrightarrow{HF} H_2N_3^+AsF_6^- \qquad (2)$$
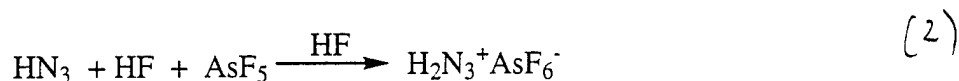
The AsF_5 required for the protonation of HN_3 to proceed could have formed by decomposition

of some $N_5^+AsF_6^-$, or less likely, by hydrolysis of $N_5^+AsF_6^-$ with traces of water in the system.

$$4N_5^+AsF_6^- + 2H_2O \longrightarrow 4HF + 4AsF_5 + 10N_2 + O_2 \qquad (3)$$
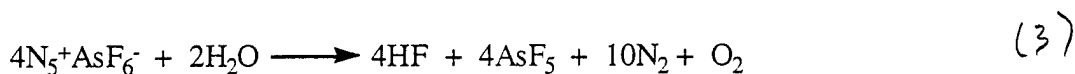
For the synthesis of ^{15}N-labeled N_5^+, ^{15}N-labeled HN_3 was prepared from stearic acid and

^{15}N-labeled $Na^+N_3^-$.

$$2Na^+\left[\overset{*}{N}_\alpha = N_\beta = N_\gamma \right]^- + 2RCOOH \longrightarrow H-\overset{*}{N}_\alpha-N_\beta-N_\gamma + H-N_\alpha-N_\beta-\overset{*}{N}_\gamma + 2Na^+RCO_2^- \qquad (4)$$

The reaction of labeled HN_3 with $N_2F^+AsF_6^-$ produced a roughly equimolar mixture of N_5^+ with

^{15}N in either the 1 or 3 positions. (structure 6)

$$N_2F^+AsF_6^- + H-\overset{*}{N}-N-N \longrightarrow \left[\begin{array}{c} \overset{*}{\overline{N}_3} \\ N_2 \quad N_2 \\ N_1 \qquad N_1 \end{array} \right]^+ AsF_6^- \qquad (6)$$

$$N_2F^+AsF_6^- + H-N-N-\overset{*}{N} \longrightarrow \left[\begin{array}{c} \overline{N}_3 \\ N_2 \quad N_2 \\ \overset{*}{N}_1 \qquad N_1 \end{array} \right]^+ AsF_6^-$$

5

The $N_5^+AsF_6^-$ salt is a white solid that is sparingly soluble in anhydrous HF. It is marginally stable at 22 °C and can be stored for weeks at -78 °C without noticeable decomposition. It can be handled both in HF solution or as a solid and, in our hands, has not exploded during careful normal handling or when squished with a stainless steel spatula at -196 °C. It has survived numerous exposures to 1.5 watt of a focused 488 nm Ar-ion laser beam at -130 °C, although a 5 mg sample did explode on one occasion with sufficient force to destroy our low-temperature Raman device. It is a powerful oxidizer, capable of igniting organic substances such as foam rubber even at low temperatures. The reaction of $N_5^+AsF_6^-$ with water is violently explosive and should be avoided. This is not surprising in view of the facts that O_2^+ is a powerful oxidizer and the first ionization potential of N_2 (359 kcal/mol) is significantly higher than that of O_2 (288 kcal/mol). The first ionization potential of N_5 or the electron affinity of N_5^+ was not calculated because of the difficulty of estimating a plausible geometry for N_5. The high energy density of N_5^+ was also confirmed by a calculation using the G2 method[13] that gave formation enthalpies of $\Delta H_f^\circ = 353$ and $\Delta H_f^{298} = 351$ kcal/mol for free gaseous N_5^+.

The solid, ^{15}N-labeled $N_5^+AsF_6^-$ in a 3 mm quartz tube was warmed in a stepwise manner from -78 to +22 °C under a vacuum of 10^{-7} torr while monitoring the volatile products with a mass spectrometer; the principal decomposition product detected was N_2. After pumping at 22 °C for 20 min, however, most of the solid remained and was identified by low-temperature Raman spectroscopy as $N_5^+AsF_6^-$, thus demonstrating that the compound has a reasonable lifetime at room temperature. In samples prepared from an excess of HN_3 and containing some $H_2N_3^+AsF_6^-$ [12] as a by-product, HN_3 and its fragments, HF, and AsF_5 were also observed in the mass spectra.

The results from a normal coordinate analysis of N_5^+ are summarized in Table 4. They show that the A_2, B_1, and B_2 vibrations and $v_1(A_1)$ are all highly characteristic, but that the symmetric N2-N3-N2· stretching mode, $v_2(A_1)$, is a mixture of stretches and bends.

The internal force constants of greatest interest are the stretching force constants f_r and f_R of the terminal and the central N-N bonds, respectively. Interpolation of the data in Table 4 and adjustments for the observed frequencies give values of 20.08 and 6.59 mdyn/Å for the terminal and the central N-N stretching force constants, respectively. The former value is significantly lower than the 22.4 mdyn/Å found for the N≡N triple bond in N_2,[15] whereas the latter value is between those found for typical N-N single (f_{N-N} = 3.6 mdyn/Å) and N=N double (f_{N-N} = 10.2 mdyn/Å) bonds.[15] The strengthening of the N-N central bonds at the expense of the terminal bonds in N_5^+, as suggested by its resonance structures, explains the relative stability of N_5^+ toward N_2 elimination. Reliable calculations of the energy barrier for N_2 elimination from N_5^+ will be the subject of a separate study.

Experimental Section

Caution! $N_5^+AsF_6^-$ is a highly energetic, strongly oxidizing material that can detonate violently. It should be handled only on a very small scale while using appropriate safety precautions (face shields, leather gloves, and protective clothing).

The $N_2F^+AsF_6^-$ was prepared from *cis*-N_2F_2 and AsF_5 as previously described.[16a-c] The HN_3 was generated by heating NaN_3 with a threefold excess of stearic acid to about 80 °C in a dynamic vacuum and collecting the evolved HN_3 in a liquid N_2 cooled trap. The HN_3 was

purified by fractional condensation through a series of -64, -95 and -196 °C traps, with the material retained at -95 °C being used. Singly ^{15}N-labeled NaN$_3$ (Cambridge, Isotope Laboratories, 99% ^{15}N label) was used for the preparation of a roughly 50/50 mixture of HN$_3$ that was singly ^{15}N-labeled in either the α or γ position. The HF (Matheson Co.) was dried by storage over BiF$_5$.[17]

The HN$_3$ was generated and handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. The HF was handled on a previously described[18] stainless steel-Teflon FEP vacuum line. The N$_5^+$AsF$_6^-$ samples were handled at -196 °C in the dry N$_2$ atmosphere of a glove box.

Low-temperature Raman spectra were recorded on a Cary Model 83GT spectrometer using the 488 nm line of an Ar-ion laser for excitation, a previously described cooling device[19], and 3 mm o.d. quartz tubes as sample containers. For measurements of the ^{14}N-^{15}N isotopic shifts, the signal was scale expanded on an external strip chart recorder. The low-temperature infrared spectra were recorded on a Mattson Galaxy FTIR spectrometer using a demountable low-temperature cell equipped with CsI windows. The ^{14}N and ^{15}N NMR spectra were recorded at 36.13 and 50.69 MHz, respectively, on a Bruker AMX 500 spectrometer using saturated solutions of N$_5^+$AsF$_6^-$ in HF/AsF$_5$ at -63 °C and heat-sealed 5 mm Teflon-FEP liners (Wilmad Glass Co.) as sample containers, delay times of 60 to 120 sec for the recording of the ^{15}N spectra, and neat CH$_3$NO$_2$ and aqueous ^{15}N-urea referenced as δ = -305.0 ppm relative to CH$_3$NO$_2$ as external standards. The spectra were recorded both hydrogen-coupled and -decoupled as a precaution against the Nuclear Overhauser Effect.

Preparation of $N_5^+AsF_6^-$. In a typical experiment, $N_2F^+AsF_6^-$ (1.97 mmol) was loaded in the drybox into a 0.75 inch o.d. Teflon-FEP ampule that was closed by a stainless steel valve. On the metal vacuum line, anhydrous HF (~ 3 mL) was added at -196 °C and the mixture was warmed to room temperature to dissolve the $N_2F^+AsF_6^-$. The ampule was connected to the glass line, and HN_3 (2.39 mmol) was added at -196 °C. The ampule was reconnected to the metal line and allowed to warm to -78 °C, where it was kept for 3 days with occasional gentle agitation. The ampule was then cooled to -196 °C to check for the presence of volatile products. Nitrogen (0.76 mmol) was identified by mass spectroscopy. All material volatile at -64 °C was pumped off for 8 h leaving behind a white solid residue that was identified by low-temperature vibrational and $^{14}N/^{15}N$ NMR spectroscopy as a mixture of $N_5^+AsF_6^-$ (~80 mol%) and $H_2N_3^+AsF_6^-$ (~20 mol%).

Preparation of ^{15}N-labeled $N_5^+AsF_6^-$. The procedure was identical to that used for the synthesis of unlabeled $N_5^+AsF_6^-$ except for using a mixture of HN_3 that was ^{15}N-labeled in either the Nα or Nγ position.

Computational Methods. Hartree-Fock (HF), density-functional theory (DFT), and single- and double-excitation coupled cluster calculations[20] that include a non-iterative treatment of connected triple excitations, denoted CCSD(T),[21] were carried out employing several atomic basis sets. The DFT calculations employed the B3LYP functional.[22] Geometries, infrared and Raman spectra, and nuclear magnetic resonance (NMR) shieldings were calculated for N_5^+ as well as, for calibration purposes, N_2F^+, $H_2N_3^+$, and the standard CH_3NO_2, the geometries and NMR parameters of which are experimentally known.[12, 14, 16] The vibrational spectra reported in this work were computed using the 6-311+G(2d) atomic basis set.[23]

The NMR shieldings were computed at the CCSD(T)/6-311+G(2d) geometries employing the gauge-including atomic orbital (GIAO) solution to the gauge-invariance problem[24] and density matrices obtained from second-order many-body perturbation theory [MBPT(2)], CCSD, or CCSD(T) calculations.[25-27] The results reported in this work used quadruple-zeta plus polarization (QZP) atomic basis sets derived from the QZ sets of Schäfer et al.,[28] supplemented with a d function with exponent 1.0. As discussed by Gauss and Stanton,[25-27] the accurate calculation of nitrogen NMR shieldings frequently requires an extensive electron correlation treatment such as that provided by the CCSD(T) method. Hartree-Fock and even MBPT(2) shielding calculations for species such as N_5^+ with many free valence electron pairs, yield extremely poor results. The GAMESS,[29] Gaussian,[30] and ACES II[31] program systems were used for these calculations on IBM RS/6000 work stations.

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Diagram Captions

Figure 1. Optimized geometries of N_5^+ calculated at the B3LYP/ and CCSD(T)/6-311+G(2d) levels of theory. Values given in parentheses are the B3LYP values.

Figure 2. Nitrogen NMR data for an equimolar mixture of singly ^{15}N-labeled $[^{15}N^{14}N^{14}N^{14}N^{14}N]^+$ and $[^{14}N^{14}N^{15}N^{14}N^{14}N]^+AsF_6^-$ recorded at -63 °C in anhydrous HF solution that was acidified with 2 mol% AsF_5. The resonance marked by an asterisk is due $H_2N_3^+$ (see text).

Figure 3. Low-temperature Raman spectrum of unlabeled solid $N_5^+AsF_6^-$.

Figure 4. Low-temperature Raman spectrum of an equimolar mixture of solid $[^{15}N^{14}N^{14}N^{14}N^{14}N]^+$ and $[^{14}N^{14}N^{15}N^{14}N^{14}N]^+AsF_6^-$.

Table 1. Observed and Calculated Nitrogen NMR Data for N_5^+

| | chemical shifts,[a] ppm | | | | |
| | observed[b] | | calculated,[c] CCSD(T)/QZP | | |
	^{15}N	^{14}N	N_1	N_2	N_3
$[^{15}N_1 - {}^{14}N_2 - {}^{14}N_3 - {}^{14}N_{2'} - {}^{14}N_{1'}]^+$	-237.3				
		-165.3[d]	-235	-166	-95
$[^{14}N_1 - {}^{14}N_2 - {}^{15}N_3 - {}^{14}N_{2'} - {}^{14}N_{1'}]^+$	-100.4				

(a) Chemical shifts are given relative to neat CH_3NO_2 as external standard. (b) The spectra were recorded hydrogen-coupled at −63 °C in anhydrous HF solution which was acidified with AsF_5. (c) An empirical correction of −20 ppm was applied to all calculated values, based on a comparison between the calculated and observed shifts of a number of closely related molecules and ions. (d) The other two resonances are badly exchange broadened and were not detected in the ^{14}N spectrum.

Table 2. Low-temperature Raman and Infrared Spectra of Solid $^{14}N_5^+$ AsF_6^- and Their Assignments Compared to the Calculated Harmonic Frequencies of Free Gaseous N_5^+

observed freq, cm^{-1} (rel intens)		assignt (point group)		calcd freq^a, (intens)^b	
Raman	IR	$^{14}N_5^+(C_{2v})$	$AsF_6^-(O_h)$	B3LYP	CCSD(T)
-130°C	-196°C				
2271 [44]	2270 m	$\nu_1(A_1)$		2336 (22)	2229 (13) [215]^c
2211 [8]	2210 s	$\nu_7(B_2)$		2282 (147)	2175 (105) [42]
	1088 s	$\nu_8(B_2)$		1167 (141)	1032 (138) [2]
871 [7]	872 w	$\nu_2(A_1)$		850 (4)	818 (0.5) [5]
	704 vs		$\nu_3(F_{1u})$		
686 [100]	680 sh		$\nu_1(A_{1g})$		
672 [17] ⎫ 669 [18] ⎭		$\nu_3(A_1)$	or part of $\nu_1(A_{1g})$ or $\nu_3(F_{1u})$	678 (1)	644 (2) [1]
579 [16]	575 w		$\nu_2(E_g)$		
		$\nu_5(A_2)$		502 (0)	475 (0) [1]
	420 sh	$\nu_6(B_1)$		424 (7)	405 (6) [0]
		$\nu_9(B_2)$		436 (0.6)	399 (1) [0.5]
	394 vs		$\nu_4(F_{1u})$		
372 [32]	380 sh ⎫ 360 sh ⎭		$\nu_5(F_{2g})$		
209 [44]		$\nu_4(A_1)$		193 (0.5)	181 (0.3) [6]
127 [55]		lattice vibration			

(a) Using a 6-311 + G(2d) basis set. (b) IR intensities (given in parentheses) in km/mol; Raman intensities [given in brackets] in Å^4/amu.   (c) The Ra intensities were calculated at the RHF level.

Table 3. Comparison of the Calculated (B3LYP) and Observed [15]N Isotopic Shifts for N_5^+

N$_5^+$ Isotopomer

N(1)-N(2)-N(3)-N(2)-N(1)					$v_4(A_1)$	$v_6(B_2)$	$v_6(B_1)$	$v_5(A_2)$	$v_1(A_1)$	$v_2(A_1)$	$v_8(B_2)$	$v_3(B_2)$	$v_1(A_1)$
								calculated frequencies (shifts), cm^{-1}					
14	14	14	14	14	193.1(0)	424.1(0)	436.3(0)	502.4(0)	678.1(0)	850.0(0)	1116.9(0)	2281.7(0)	2336.3(0)
14	14	15	14	14	191.8(1.3)	422.0(2.1)	436.0(.2)	502.4(0)	677.5(.7)	833.3(16.7)	1138.0(28.9)	2281.2(.5)	2336.3(.1)
15	14	14	14	14	190.8(2.2)	422.3 (1.8)	434.7(1.5)	500.7(1.7)	674.4(3.7)	847.4(2.6)	1163.4(3.5)	2259.8(21.9)	2324.5(11.9)

observed frequencies (shifts),cm^{-1}

	$v_2(A_1)$		$v_3(B_2)$		$v_1(A_1)$	
	IR	RA	IR	RA	IR	RA
	872(0)	871(0)	2210(0)	2211(0)	2271(0)	2271(0)
	858(14)	855(16)	2209.8	2211(1)	2270.8	2271(0)
	870(2)	869(2)	2189.0(21)	2190(21)	2259.0(12)	2259(12)

Table 4. Results from the Normal Coordinate Analysis[a] of N_5^+

approx mode description in point group C_{2v}			frequency, cm^{-1}		symmetry force constants[b], CCSD(T) (B3LYP)					potential energy distribution[a], %
			obsd	calcd CCSD(T) (B3LYP)		F_{11}	F_{22}	F_{33}	F_{44}	CCSD(T)
A_1	υ_1	in phase terminal stretches	2270	2229 (2336)	F_{11}	19.573(21.314)				93(1) + 6(2)
	υ_2	sym central stretch	872	818 (850)	F_{22}	0.702(0.843)	5.546(6.952)			62(2) + 23(3) + 13(4) + 2(1)
	υ_3	central bending		644 (678)	F_{33}	-0.085(-0.137)	1.377(1.535)	1.540(1.427)		39(3) + 33(2) + 23(4) + 5(1)
	υ_4	in phase terminal bends	209	181 (193)	F_{44}	0.167(0.171)	0.204(0.312)	0.120(0.108)	0.373(0.425)	64(4) + 37(3) - 1(2)
A_2	υ_5	torsion		475 (502)	F_{55}	0.0266(0.0281)				100(5)
B_1	υ_6	torsion		405 (424)	F_{66}	0.0236(0.0246)				100(6)
B_2	υ_7	out of phase term stretch	2210	2175 (2282)	F_{77}	19.491(21.272)				96(7) + 4(8)
	υ_8	asym central stretch	1088	1032 (1167)	F_{88}	1.197(1.359)	4.780(5.927)			95(8) + 4(7)
	υ_9	out of phase terminal bends		399 (436)	F_{99}	0.200(0.195)	0.085(0.159)	0.358(0.423)		99(9) + 1(8)

(a) The following symmetry coordinates were used for [N1-N2-N3-N2'-N1']$^+$: $S_1=v(1-2)+v(1'-2)$; $S_2=v(2-3)+v(2'-3)$;

$S_3=\delta(2-3-2')$; $S_4=\delta(1-2-3)+\delta(1'-2'-3)$;

$S_5=\tau(1-2-3-2')+\tau(2-3-2'-1')$; $S_6=\tau(1-2-3-2')-\tau(2-3-2'-1')$; $S_7=v(1-2)-v(1'-2)$; $S_8=v(2-3)-v(2'-3)$; $S_9=\delta(1-2-3)-\delta(1'-2'-3)$. (b) The two most important internal force constants, estimated from the calculated symmetry force constants and the observed frequencies are $f_{(1-2)}=20.08$ mdyn/Å and $f_{(2-3)}=6.59$ mdyn/Å. Streching constants in mdyn/Å, deformation constants in mdyn/Å/rad^2, and stretch-bend interaction constants in mdyn/rad.

(166.7°)
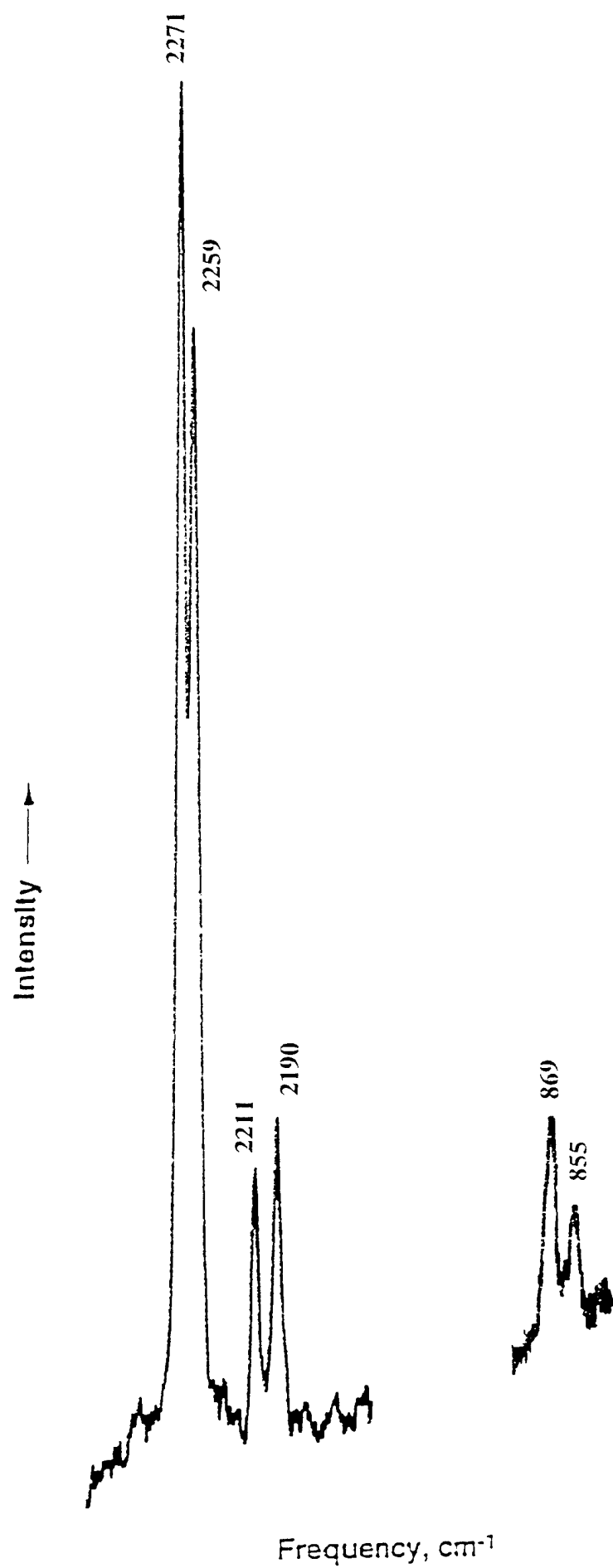166.4°

108.3°
(112.3°)

1.33
(1.30)

1.12
(1.11)

Intensity →

Frequency, cm⁻¹

2271
2211
871
672 669
579
686
372
209

Intensity ——▶

2271

2259

2211

2190

869

855

Frequency, cm⁻¹
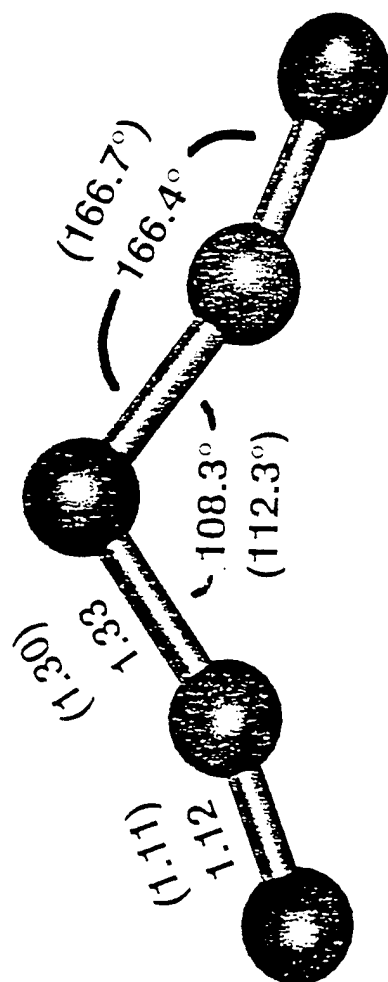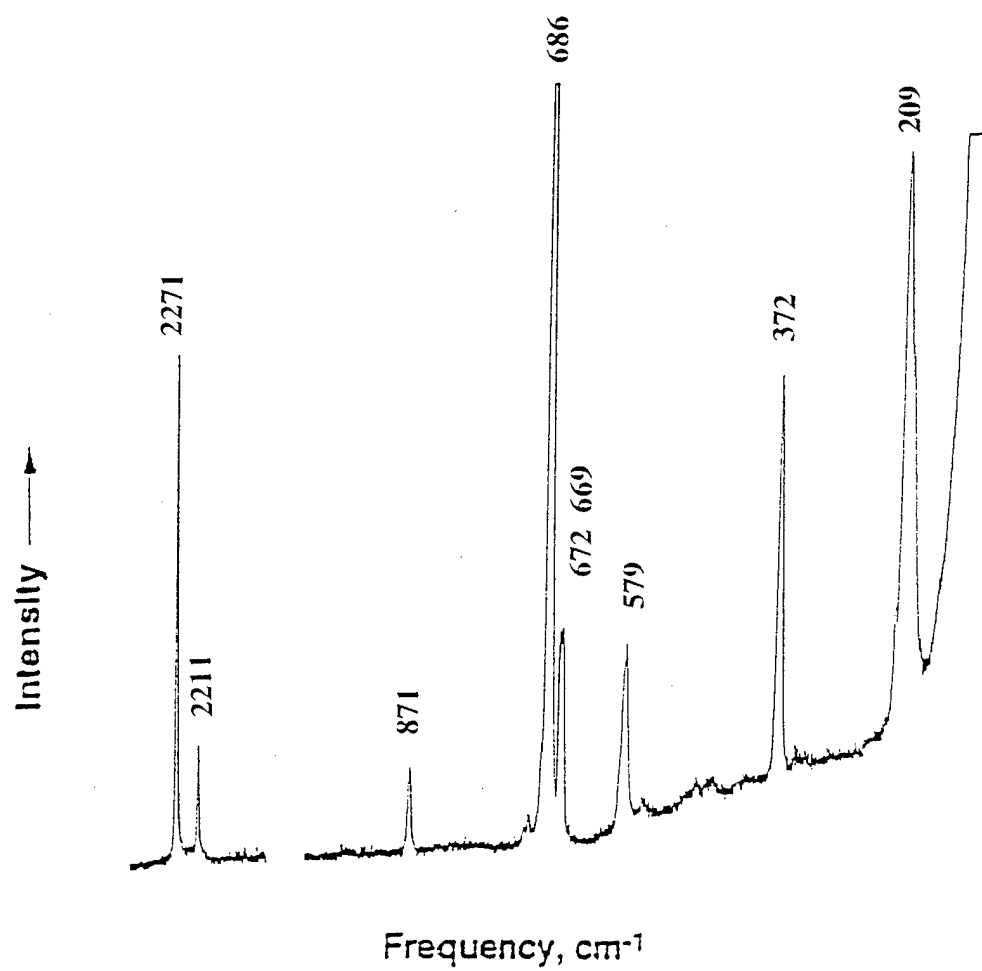
Table 1											
Mechanical Properties of Class 1.3 Boost Propellants vs. Castor 120®											
Propellant	**91% Solids**			**90% Solids**			**89% Solids**			**Castor 120® 88% Solids**		
Test, Condition*	1	2	3	1	2	3	1	2	3	1**	2	3
Modulus (psi)	4210	1106	396	2220	526	312	2490	475	256	4950	840	465
σ_m **(psi)**	561	141	64	501	121	74	529	116	68	795	142	83
$\sigma_m^{t,c}$ **(psi)**	685	165	75	695	167	97	774	164	98	1135	227	110
$\varepsilon_m^{t,c}$ **(%)**	22	18	17	41	39	32	52	45	45	47	63	34

* 1 = 20°F, 20 ipm, 1000 psi; 2 = 75°F, 2 ipm, 1 atm; 3 = 135°F, 0.02 ipm, 1 atm

**Data interpolated from Castor 120® propellant measurements at 5, 40, 75, 110°F

Table 2		
Mechanical Properties of 89 Percent Solids, HX-752 and Tepanol Propellants		
Property (75°F, 2 ipm)	**HX-752 Formulation**	**Tepanol Formulation**
Modulus (psi)	888	585
σ_m **(psi)**	196	144
$\sigma_m^{t,c}$ **(psi)**	270	210
ε_m^{t} **(%)**	37	43
$\varepsilon_m^{t,c}$ **(%)**	40	49
ε_f^{t} **(%)**	42	51